

THE MOLECULAR WEIGHT BETWEEN CROSSLINKS OF SELECTED AMERICAN COALS

Lucy M. Lucht¹ and Nikolaos A. Peppas²

School of Chemical Engineering
Purdue University
West Lafayette, Indiana 47907

INTRODUCTION

Van Krevelen (1961) and Sanada and Honda (1966, 1967) were the first to propose that the organic portion of bituminous coals can be considered as a "crosslinked polymer" (sic). Since then, Larsen and Kovac (1978), and Lucht and Peppas (1981a) have developed mathematical, topological, and physicochemical models which describe network structure of coals by accurate and physically complete theories.

Lucht and Peppas (1981a) proposed that the organic phase of coal consists of a crosslinked macromolecular structure which does not dissolve at low temperatures unless reaction and degradation occur; and of a portion of uncrosslinked macromolecular chains of predominately aliphatic character, which can be extracted at low or moderate temperatures if an appropriate solvent is used. These uncrosslinked molecules may be material from the original matter formed during diagenesis, or partially degraded chains that were formed through depolymerization reactions during the development of coal. Figure 1 shows a simplified description of the organic phase according to Lucht and Peppas. The same scheme includes not only ideal chemical crosslinks (A,B) but also unreacted functionalities (C), chain ends (D), and various defects of the macromolecular structure such as loops (F) and physical crosslinks (E), known as entanglements. Physical crosslinks occur because the system is highly entangled, that is the chains are rigid and have limited mobility. Hence, they are unlikely to disentangle when stressed or swelled. Chemical crosslinks are formed by chemical reaction of two or more chains to yield a multifunctional crosslink.

The chemical nature of the crosslinks found in coal has not been adequately determined. In the development of mathematical models to describe the behavior of the network, crosslinks are assumed to be points or short bridges with a molecular weight much smaller than M_c . Here M_c refers to the statistical number average molecular weight between crosslinks of the coal structure. Obviously, as M_c increases the degree of crosslinking decreases.

To further simplify the macromolecular structure in order to make it tractable for statistical analysis, Lucht and Peppas (1981b) proposed a crosslinked coal structure, where the crosslinks are bonding regions similar to groups proposed by Wiser (1977) (see Figure 2). Each chain consists of groups of aromatic clusters and connecting bonds. The cluster may be a structure of two or more aromatic or heterocyclic rings fused together, whereas the connecting bonds are simple groups such as -O-, -S-S- and -CH₂-. In addition, the macromolecular chains which constitute a large portion of the coal do not exhibit a repeating unit, as defined in conventional polymers. Thus, coal does not have a "polymer structure" but a *macromolecular structure*.

The unfortunate use of the term "polymeric structure" by Van Krevelen (1961), has created some confusion, not only among coal scientists, who try to analyze the crosslinked structure, but also among polymer scientists, who try to apply statistical mechanical theories. A hypothetical repeating unit may be defined, solely for purposes of application of topological, statistical mechanical, and swelling theories, for the determination of M_c .

Experimental techniques which support the existence of a crosslinked structure are based on extraction and swelling of the coal sample or coal matrix with thermodynamically "good" solvents such as pyridine and ethylene diamine, and thermodynamically

1. Present address: Lawrence Livermore Laboratory, P.O. Box 808, Livermore, CA 94550.

2. Corresponding author.

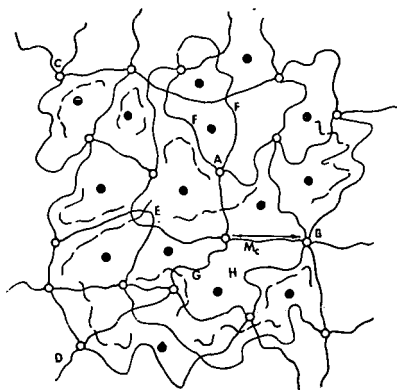
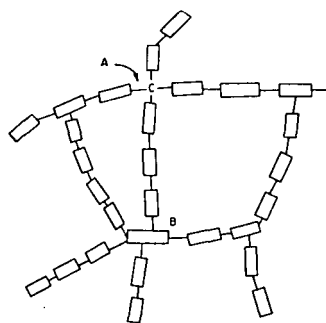


Figure 1. Simplified Representation of the Crosslinked Structure of Coal Including Possible Defects. —: Chains participating in network structure; ----: extractable (unreacted or degraded) chains; o: crosslinks (junctions); •: molecules of swelling agent; \bar{M}_c : molecular weight between crosslinks; A: tetrafunctional crosslink; B: multifunctional crosslink; C: unreacted functionalites; D: chain end; E: entanglement; F: chain loop; G: effective network chain; H: mesh size.



Proposed Crosslinked Structure in Coals.

- Aromatic ring cluster
- Connecting band
- A Tetrafunctional crosslink
- B Multifunctional crosslink

Figure 2. Proposed Crosslinked Structure in Coals According to Lucht and Peppas (1981).

"poor" solvents such as methanol, benzene, ethanol, etc. Most of the studies have been performed using either Soxhlet extraction, or simple or sophisticated dynamic swelling experiments. The term "solvent" is used here interchangeably to describe liquids which dissolve coal, and also liquids which swell it or react with it.

Here we present recent experimental results which characterize the organic phase of coal in terms of parameters of the crosslinked structure.

EXPERIMENTAL PART

Coal samples which had been ground to an average particle size of 20-30 mesh (600-850 μm) and packed under nitrogen were furnished by the coal bank of Pennsylvania State University.

Extraction was used to separate the coal matrix from material which is free or loosely held in the interstices. In a typical extraction, a coal sample of 20-30 mesh particle size and approximately 3 g. was weighed to ± 0.0001 g, and extracted in a Soxhlet apparatus using pyridine (Aldrich) under nitrogen at 115.5°C . The extract solution was replaced every one to four days with fresh pyridine until the extract solution appeared to be pure pyridine (usually one to eight weeks). The extracted residue was dried to constant weight under vacuum at $\text{ca } 60^\circ\text{C}$ and $\text{ca } 0.93$ MPa under flowing nitrogen.

Equilibrium swelling studies were conducted to provide the final values of the equilibrium volume fraction of coal in a solvent-swelled system at a specified swelling temperature. Data were collected via gravimetric sorption studies. Samples were dried at 60° to 80°C under flowing nitrogen at slightly greater than atmospheric pressure for at least 24 hours to remove free surface water. Prewighed samples were exposed to an environment saturated with vapors of pyridine in dessicators at specified temperatures, maintained constant either with a water bath or with a convection oven. The time required for swelling equilibrium was between 5-12 weeks. At the end of the swelling period, the samples were removed and reweighed.

RESULTS AND DISCUSSION

Equilibrium swelling studies provide the final values of the equilibrium volume fraction of coal in a solvent-swelled system, v_2 , at a specified swelling temperature. The degree of swelling, $Q = 1/v_2$, is an indicator of both solvent/coal thermodynamic interactions and of the physicochemical structures of coal. It can be used in any Gaussian or modified Gaussian network equation such as equation (1) to determine \bar{M}_c and other crosslinking parameters. In addition, results can be used to quantify favorable thermodynamic interactions with a solvent for liquefaction purposes.

$$\frac{1}{\bar{M}_c} = \frac{\frac{v_2}{V_1} [\ln(1 - v_2) + v_2 + \chi v_2^2] [1 - \frac{1}{N} v_2^{2/3}]^3}{[\frac{1}{2} v_2 - v_2^{1/3}] [1 + \frac{1}{N} v_2^{1/3}]^2} \quad (1)$$

Here, \bar{M}_c is the number average molecular weight between crosslinks; \bar{v} is the specific volume of the macromolecule; V_1 is the molar volume of the swelling agent; v_2 is the volume fraction of the macromolecule in the swollen system; χ is the Flory-Huggins thermodynamic interaction parameter; and N is the number of bond vectors in a single chain, given by equation (2) where M_r is the molecular weight of the characteristic repeating unit.

$$N = \frac{\bar{M}_c}{M_r} \quad (2)$$

Equation (1) was developed specifically for application to the equilibrium solvent swelling of coals. This approach accounts for the finite expansion of solvent-swelled coals by limiting the extensibility of the individual chain. It is therefore more appropriate for determination of the molecular weight between crosslinks, \bar{M}_c , via solvent-swelling studies, than the Flory-Rehner equation, which assumes that the end-to-end distance between chain ends is much less than the contour length of the chain and thus allows a chain to be infinitely extensible.

It must be noted that in our proposed model (Figure 2), a repeating unit consists

of a cluster and a connecting bond. This is a reasonable assumption in view of the comparatively small size of the connecting bond (usually $-\text{CH}_2-$, $-\text{S}-$, or $-\text{O}-$) with respect to the cluster size. The molecular weight of a repeating unit is about 130 for lignites, 170 for bituminous coals up to 86% C (dmmf), and 370 for coals with a higher carbon content.

Pyridine was used as the probe for most experiments because it is one of the few solvents which causes significant swelling in all but the highest rank coals; some researchers (e.g., Marzec *et al.*, 1979) believe that pyridine has a stronger interaction with coal than the extractables and that pyridine may be able to destroy hydrogen-bonding in the coal structure.

Figure 3 is a typical graph of results showing the dependence of the degree of swelling, Q , corrected for mineral matter on carbon content (on a dmmf basis). It was assumed that the organic vapor does not swell clays or metals to a significant degree, so their weight was subtracted from the total. Pyridine vapor swelling was conducted at $35.0 \pm 0.5^\circ\text{C}$ for 60 days to swelling equilibrium and compared with the data obtained, as described above, over 51 days at $60 \pm 0.5^\circ\text{C}$. The degree of swelling is significantly greater at 60°C than at 35°C , although the shapes of the curves are similar. At 35°C , the degree of swelling is constant at $Q = 1.8$ - 2.0 from ca 70% C and up to approximately 86% C, dropping as in the higher temperature case to $Q = 1.1$ at 91% C.

Experimental data were also obtained which show the effect of pyridine pretreatments on the solvent vapor swelling of coals. Equilibrium swelling of these samples was performed at $60 \pm 0.5^\circ\text{C}$ for 51 days and these data are shown in Figure 4. The shape of the curve is similar to that of the unextracted coals swelled by pyridine as shown in Figure 3, although the magnitude of the degree of swelling in the pyridine extracted coals over the carbon content range of 69.94 to 82.48% C (dmmf) is somewhat lower than for the unextracted coals, ranging from $Q = 2.2$ to 2.5 for the pyridine extracted coal samples as compared to $Q = 2.5$ to 2.8 for the untreated coal samples.

ANALYSIS

The modified Gaussian network equation (1) can be applied only to the results of swelling of coal networks which are free of uncrosslinked material, i.e., extractable material. Thus, only the results from the equilibrium swelling of pyridine-extracted coal samples were used in the determination of the molecular weight between crosslinks.

In the determination of the molecular weight between crosslinks, the volume fraction of coal in the pyridine swollen system, $v_2 = 1/Q$, was calculated on a mineral matter free basis, assuming that pores with diameter of greater than 50 Å contained condensed solvent only which did not contribute to swelling. The values of these pore volumes were determined by mercury porosimetry.

The average values of the molecular weight of a hypothetical repeating unit of coal were taken to be 130 for lignite or sub-bituminous coal samples, 170 for bituminous coal samples with carbon contents up to ca 86% C (dmmf), and 370 for all coal samples of rank greater than medium volatile bituminous up to semi-anthracite samples. These values were determined from the present view of the size of the aromatic/hydroaromatic clusters and their crosslinks.

The values of the thermodynamic interaction parameter, χ , for coals with carbon contents of 75.9, 82.4, and 88.2% C (dmmf) were determined by the Hildebrand-Skatchard regular solution theory from the solubility parameters determined by Kirov *et al.*, (1967). The values of the solubility parameter reported in that study were determined at 25°C , while the equilibrium swelling experiments of our work were carried out at 35, 60 and 80°C . Therefore, corrections in the solubility parameter values were made for different temperatures in the following way.

The dependence of the effective number of repeating units between crosslinks, N , on carbon content is shown in Figure 5 while the dependence of the effective molecular weight between crosslinks, \bar{M}_c , on carbon content is shown in Figure 6. Results from equilibrium swelling by pyridine vapor at 35°C of pyridine extracted coals were used in the application of equation (1).

The number of repeating units between crosslinks is relatively constant, ranging from $N = 7.0$ to 8.5 , over the carbon content range of 69.96 to 82.48% C (dmmf). At a carbon content of 86.01% C (dmmf), the value of N drops to 4.6 and continues to decline

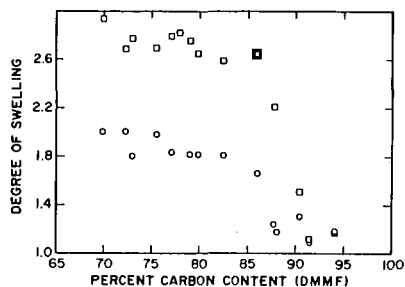


Figure 3. Equilibrium Swelling by Pyridine Vapor of 20-30 mesh, Untreated Coal Particles. (□) 60°C; (○) 35°C.

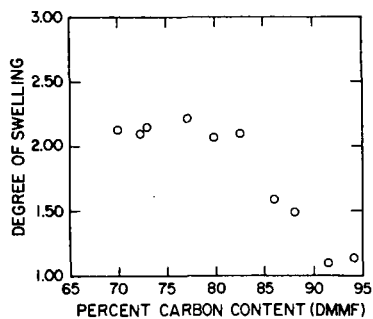


Figure 4. Equilibrium Swelling by Pyridine Vapor of 20-30 mesh, Pyridine-Extracted Coal Particles at 60°C.

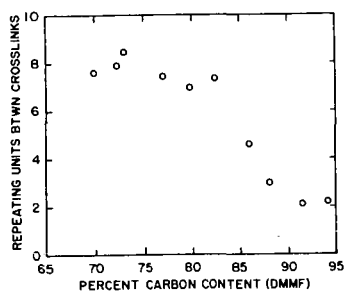


Figure 5. Dependence of Number of Repeating Units Between Crosslinks on Carbon Content of Coal Sample.

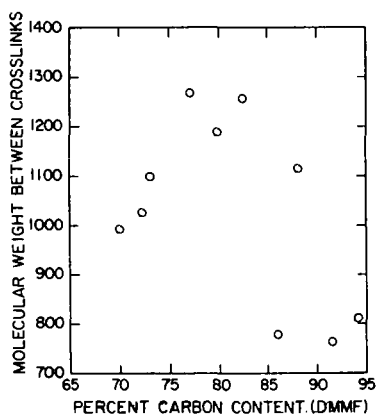


Figure 6. Dependence of Molecular Weight Between Crosslinks on Carbon Content of Coal Sample.

to a value of 2.2 at a carbon content of 91.54%C (dmf).

Nelson (1983) obtained solvent uptake data for methanol vapor into coal over a range of activities of methanol and then applied modification and rearrangements of the Flory-Rehner network swelling equation and of the modified Gaussian network equation (1) to these results. The modification he made was to assume that the swollen coal system was infinitely dilute in coal, and thus the volume fraction of solvent could be approximated as the activity of the solvent. This is obviously an invalid approximation as the volume fraction of coal in a methanol swelled coal system is on the order of 0.7. He also assumed in his determination of the molecular weight between crosslinks that the number of repeating units between crosslinks was about 7. This defeats the purpose of the modified Gaussian equation, which is to elucidate the effective flexibility or number of repeating units between crosslinks. It is the size of the repeating unit which must be known or estimated. The values of the molecular weight between crosslinks determined by Nelson for swelling by methanol were ca 70 and ca 120, using the Flory-Rehner and modified Gaussian equations, respectively.

Equilibrium swelling results of pyridine extracted coals in pyridine liquid at room temperature were obtained by Kirov *et al.* (1967). The research group of Sanada and Honda (1966) performed equilibrium swelling of pyridine extracted coals with pyridine vapor at room temperature. Both groups used their data in the Flory-Rehner Gaussian equation. The results have been recalculated (Larsen and Kovac, 1978; Lucht and Peppas, 1981a) to correct some errors in the initial work of Sanada and Honda and to convert the values of volume between crosslinks determined by Kirov *et al.* to the more commonly used molecular weight between crosslinks.

The values of M_c determined by us from the data of Kirov *et al.* are 2595, 2100 and 940 for coals with carbon content of 75.9, 82.4 and 88.2%C (daf). The magnitude of the values M_c are approximately twice those of our values, which could result from an apparent high degree of swelling due to solvent between particles in the liquid equilibrium swelling procedure used. Our corrected results of the data of Sanada and Honda range from M_c equal to zero (a large negative number) to about 15,000, although many of their values of M_c range from 700 to 2000. The unreasonable values of M_c result from the values they used of the thermodynamic interaction parameter, χ , obtained from the results of osmotic pressure data for pyridine extractables of Wynne-Jones *et al.* (1952). When the value of χ increases for a given set of conditions, the value of M_c will also increase until χ reaches a certain critical value, beyond which the Gaussian and the modified Gaussian equations predict a negative molecular weight between crosslinks. Rephrased, it is impossible to have simultaneously a high degree of swelling and unfavorable interaction between a solvent and the macromolecule being swelled.

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